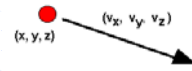


Physical Chemistry

Lecture 10
Mathematics of Quantum
Mechanics

Classical mechanics and states

- In mechanics, one describes
 - Where particles are
 - Where particles are going subject to forces
- The **state** of a system is completely defined by the positions and momenta of all particles -- the **trajectories**
- Everything is absolutely determined by forces and initial conditions



$$v(t) = v(0) + \frac{1}{m} \int_0^t F(t') dt'$$

$$r(t) = r(0) + \int_0^t v(t') dt'$$

Hamiltonian mechanics

- Newton's mechanics (which most of you learned in physics) does not show clearly the connection to quantum mechanics
- Hamiltonian mechanics (developed by Sir William Cayley Hamilton) is convenient and shows the connection
- Hamiltonian function
 - Energy as a function of position and momentum of particles

Finding the Hamiltonian function of a system

- Express energy as a function of **momenta** and **co-ordinates** only
- Example: A particle in a Morse potential along the x direction of a co-ordinate system

$$V_{Morse}(x) = D_e [1 - \exp(-\beta(x - x_e))]^2$$

$$H = T + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + D_e [1 - \exp(-\beta(x - x_e))]^2$$

Hamilton's canonical equations

- Canonical equations give the equations of motion of a conservative system

$$\frac{\partial H}{\partial p_k} = \frac{\partial x_k}{\partial t} \quad \text{and} \quad \frac{\partial H}{\partial x_k} = -\frac{\partial p_k}{\partial t}$$

- Change of a parameter defined in terms of the **Poisson bracket**

$$\frac{\partial A}{\partial t} = \{A, H\} = \sum_k \left(\frac{\partial A}{\partial x_k} \frac{\partial H}{\partial p_k} - \frac{\partial A}{\partial p_k} \frac{\partial H}{\partial x_k} \right)$$

Example Hamiltonian problem

- Particle in gravitational field along the z direction
- Kinetic energy = $mv^2/2$
- Potential energy = mgz

$$H = K.E. + P.E. = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz$$

- Canonical equations give equations of motion
 - Equations for x and z motion shown
 - Equation for y motion similar to x motion
- Equations for trajectories can be solved directly by integration

$$\begin{aligned} \frac{\partial H}{\partial p_z} &= \frac{\partial z}{\partial t} = \frac{p_z}{m} \\ \frac{\partial H}{\partial z} &= -\frac{\partial p_z}{\partial t} = mg \\ \frac{\partial H}{\partial p_x} &= \frac{\partial x}{\partial t} = \frac{p_x}{m} \\ \frac{\partial H}{\partial x} &= -\frac{\partial p_x}{\partial t} = 0 \end{aligned}$$

Conserved quantities

- ◆ Quantities that do not change in time are conserved
- ◆ Example from the gravitational-field problem

$$\frac{dp_x}{dt} = 0 \Rightarrow p_x \text{ is a conserved quantity}$$

$$\frac{dp_y}{dt} = 0 \Rightarrow p_y \text{ is a conserved quantity}$$

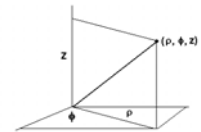
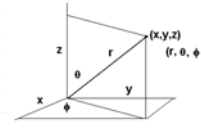
$$\frac{dp_z}{dt} \neq 0 \Rightarrow p_z \text{ is not conserved}$$

- ◆ Also called constants of motion

Co-ordinate systems

- ◆ Positions defined relative to a co-ordinate system

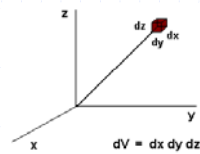
- Cartesian co-ordinates
 - ◆ (x, y, z)
- Spherical polar co-ordinates
 - ◆ (r, θ, ϕ)
- Cylindrical co-ordinates
 - ◆ (ρ, ϕ, z)
- Confocal elliptical co-ordinates
 - ◆ (u, v, ϕ)



Volume elements for integration

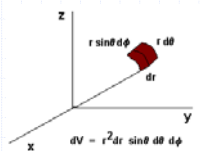
- ◆ In the cartesian representation

- $dV = dx dy dz$
- All space
 - ◆ $-\infty \leq x \leq \infty$
 - ◆ $-\infty \leq y \leq \infty$
 - ◆ $-\infty \leq z \leq \infty$



- ◆ In the spherical polar representation

- $dV = r^2 dr \sin\theta d\theta d\phi$
- All space
 - ◆ $0 \leq r \leq \infty$
 - ◆ $0 \leq \theta \leq \pi$
 - ◆ $0 \leq \phi \leq 2\pi$



Vectors and scalars

- ◆ Scalar

- A quantity having magnitude only

- ◆ Vector

- A quantity having magnitude and direction

- ◆ Functions

- Scalar function -- $f(x, y, z)$
- Vector function treated as three scalar functions:

$$\mathbf{V}(x, y, z) = V_x(x, y, z)\mathbf{i} + V_y(x, y, z)\mathbf{j} + V_z(x, y, z)\mathbf{k}$$

Vector algebra

- ◆ Two vectors are equal if the corresponding components are equal.
- ◆ The sum of two vectors is a vector with elements that are sums of corresponding elements.

$$\mathbf{C} = \mathbf{A} + \mathbf{B} \Leftrightarrow c_i = a_i + b_i$$
- ◆ The difference of two vectors is defined analogously.

$$\mathbf{C} = \mathbf{A} - \mathbf{B} \Leftrightarrow c_i = a_i - b_i$$

Vector multiplication

- ◆ Dot product (scalar or inner product)

$$\mathbf{A} \cdot \mathbf{B} = \sum_i a_i b_i$$

- ◆ Cross product (vector or outer product)

$$\mathbf{C} = \mathbf{A} \times \mathbf{B} \Leftrightarrow c_i = \varepsilon_{ijk} (a_j b_k - a_k b_j)$$

- ◆ Division of vectors is not defined.

Complex numbers and functions

◆ z represents a quantity like a two-dimensional vector

◆ Use the imaginary number

$$i = \sqrt{-1}$$

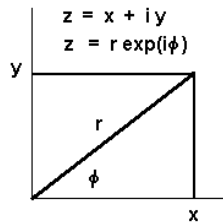
◆ Expressed as either

- The real (x) and imaginary (y) parts
- The magnitude (r) and phase (ϕ)

◆ Can depend on other variables

- Complex functions

$$z(t) = x(t) + i y(t) = r(t) \exp(i\phi(t))$$



Summary

◆ Hamiltonian functions are constructed to describe the energy of a system

- Once known, one can find equations of motion from the Hamiltonian function of a conservative system

◆ Constants of motion are conserved quantities

◆ Different co-ordinate systems describe the same system

- Can choose the co-ordinate system to define a problem so that it simplifies the mathematics
- Integration requires volume elements for each type of co-ordinate system

◆ Algebra of vectors

- Sums and differences
- Two different kinds of products